

## Viscosity and Surface Tension of Dilute Salicylic Acid-Cetrimide Systems

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**Abstract** □ The viscosity and surface tension of systems containing small amounts of salicylic acid in aqueous solutions of cetrimide were determined. An abrupt increase in viscosity was observed, and the molar ratio of salicylic acid to cetrimide at which this viscosity increase occurred was 1:2. The surface tension of these systems also increased sharply after an initial lowering. The salicylic acid concentration at which this behavior was demonstrated was almost the same as that at maximum solubility in the surfactant solution.

**Keyphrases** □ Salicylic acid-cetrimide—aqueous solutions, viscosity and surface tension □ Cetrimide-salicylic acid—aqueous solutions, viscosity and surface tension □ Viscosity—aqueous solutions of salicylic acid and cetrimide □ Surface tension—aqueous solutions of salicylic acid and cetrimide

Salicylic acid previously was found to interact with cetrimide in aqueous solutions, leading to a rise in viscosity (1). This interaction was attributed to the formation of macromolecules, and the interaction was shown to be highly specific. It is restricted to the *ortho*-hydroxy-substituted benzoic acid and does not apply to the amino, chloro, or nitro derivatives.

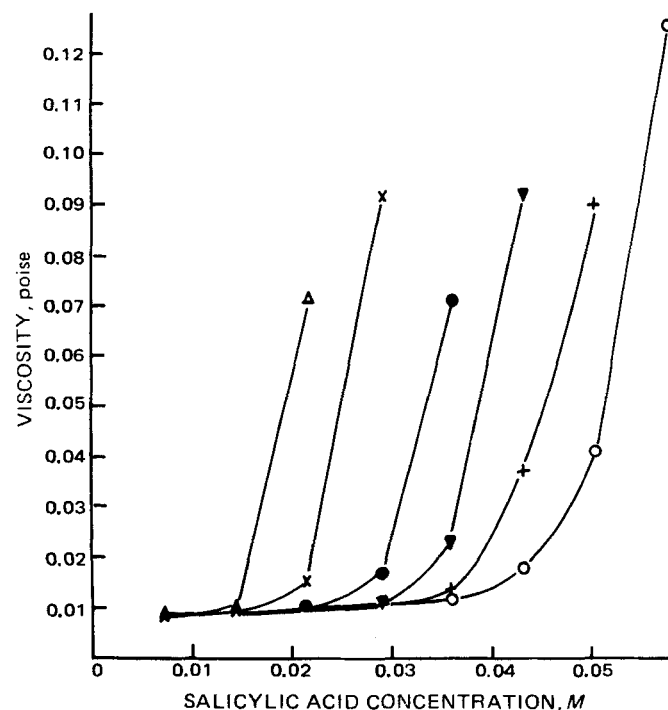
Determination of viscosity in previous studies involved the use of a viscometer that limited the lower range of viscosity measurements that could be made. Dilute concentrations of salicylic acid in cetrimide solutions produce much less viscous systems, and their viscosity can be determined using a U-tube viscometer. The purpose of this investigation was to determine whether the viscosity behavior observed in the salicylic acid-cetrimide systems studied earlier (1) also occurs in similar, but much more dilute, systems. Since the surface activity of these systems is likely to be affected by the interaction between salicylic acid and cetrimide, surface tension measurements made at the same temperature also are included.

### EXPERIMENTAL

The recrystallized salicylic acid, mp 158–159°, and cetrimide<sup>1</sup> BP used were the same as described previously (2). The viscosity was measured using a U-tube viscometer, equilibrated in a thermostatically controlled water bath at 25 ± 0.5°. The drop-weight method, employing a micrometer syringe<sup>2</sup>, was used to determine the surface tension at the same temperature.

### RESULTS AND DISCUSSION

An abrupt increase in viscosity occurred in surfactant solutions of varying concentrations when the salicylic acid content was increased (Fig.



**Figure 1**—Viscosity change in cetrimide solutions containing salicylic acid at 25°. Key [cetrimide concentration (M)]:  $\Delta$ , 0.0149;  $\times$ , 0.0298;  $\bullet$ , 0.0446;  $\blacktriangledown$ , 0.0595;  $+$ , 0.0744; and  $\circ$ , 0.0893.

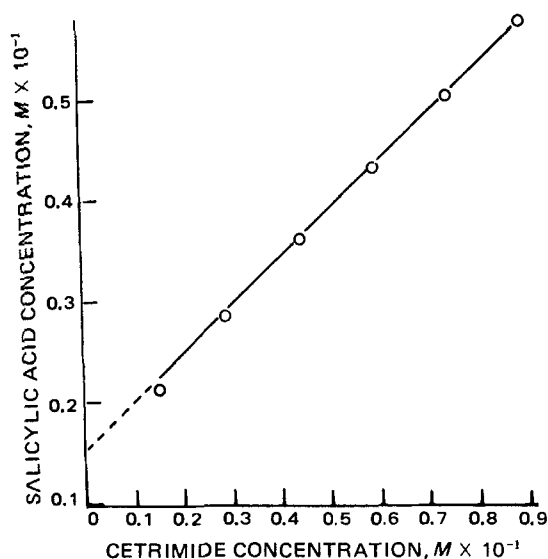
1). The sudden viscosity increase indicated that interaction took place and that macromolecules were formed. At concentrations less than 0.0149 M cetrimide in the presence of different amounts of salicylic acid, no such rise in viscosity was produced. This result may have been due to the fact that the quantities of the acid and surfactant used were small and not adequate to demonstrate this pattern of behavior. The degree of interaction produced under such conditions may be inappreciable.

Aqueous solutions of cetrimide gave rise to this viscosity change only when certain quantities of salicylic acid were present. The acid needed for this purpose increased proportionately with cetrimide concentration (Fig. 2). The molar ratio of salicylic acid to cetrimide needed for this viscosity change to occur was 1:2, as calculated from the slope of the graph in Fig. 2. In addition, as the cetrimide concentration approached zero, the corresponding concentration of salicylic acid required to cause the viscosity increase approached that of its solubility in water, *i.e.*, 0.0156 M, as determined by taking the mean between a clear aqueous solution and one in which excess salicylic acid was present.

This water solubility value was in good agreement with literature values (3–8), suggesting that the minimum amount of salicylic acid necessary to bring about an increase in viscosity must exceed that required to saturate the aqueous phase. The minimum amount of cetrimide required for the same purpose has to be greater than 0.0149 M. This surfactant

<sup>1</sup> Glovers Chemicals Ltd., Leeds 12, England.

<sup>2</sup> Agla, Burroughs Wellcome and Co., London, England.



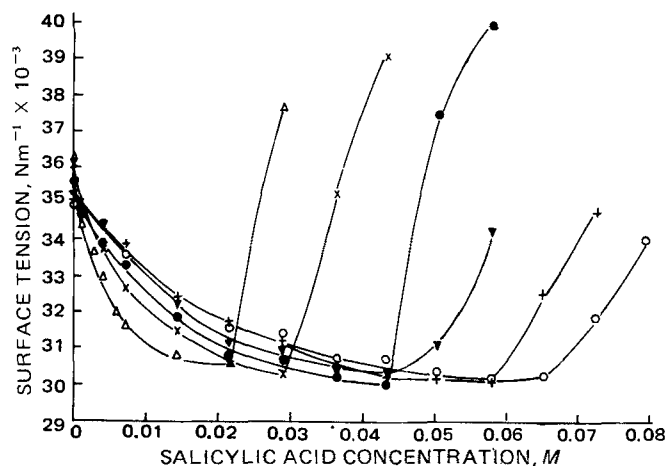
**Figure 2**—Relationship between salicylic acid concentration and cetrimide concentration at which a marked increase in viscosity occurs at 25°.

concentration is well above the critical micelle concentration (CMC), which was 0.0015 M at 25°, using the Du Nouy tensiometer<sup>3</sup>. Therefore, the interaction takes place in the presence of micelles. The molar ratio of 1:2 for salicylic acid–cetrimide suggests that twice as many of the larger size cetrimide molecules are probably involved in the interaction with one smaller size salicylic acid molecule. This effect could be associated with the two OH<sup>-</sup> groups in the acid molecule. The proximity of the OH<sup>-</sup> group to the COOH<sup>-</sup> group is essential for interaction (1).

The viscosity of the salicylic acid–cetrimide systems continued to increase after the marked viscosity change occurred until the surfactant solutions became saturated with the acid. The saturated dispersions were allowed to stand to separate the excess acid, which otherwise would interfere with the viscosity measurement, and the viscosity of the clear solution thus obtained was determined. The viscosity tended to decrease. A similar reduction in viscosity was also observed in systems containing higher concentrations of salicylic acid and cetrimide (1), except that the reduced viscosity referred to the viscosity of the saturated system (1). It was not necessary to remove the excess acid since it did not interfere with the rotation of the viscometer cylinders.

When a solution changes to a dispersion, its viscosity generally increases, particularly if the dispersed particles are mainly responsible for the viscous nature of the system. However, this generalization apparently does not apply to these saturated salicylic acid–cetrimide systems. The mesh-like network formed by the macromolecules, which result from the interaction between salicylic acid and cetrimide, is probably easily disrupted. The presence of excess salicylic acid may weaken the links and lead to a structural breakdown, so the viscosity decreases.

From the data plotted (Fig. 3), it is seen that the surface tension was initially depressed and then tended to become constant before rising. The amount of salicylic acid giving this sharp rise in surface tension was slightly greater than that causing the viscosity rise in corresponding systems. The particular acid concentrations responsible for this effect



**Figure 3**—Change in surface tension of cetrimide solutions containing varying amounts of salicylic acid at 25°. Key [cetrimide concentration (M)]: Δ, 0.0149; ×, 0.0298; ●, 0.0446; ▼, 0.0595; +, 0.0744; and ○, 0.0893.

were about the same as the concentration of salicylic acid at maximum solubility in the respective surfactant solution. With cetrimide concentrations lower than 0.0149 M and in the presence of different quantities of salicylic acid, this pattern of surface tension changes was not obvious, indicating that the surface activity of the system is only affected if there is an appreciable degree of interaction.

The fall in surface tension at a low salicylic acid concentration may be brought about by the salicylic acid interacting with the cetrimide molecules adsorbed at the interface in preference to those in the bulk of the system, thereby affecting the interfacial packing. As the concentration of salicylic acid is increased, fewer interfacially adsorbed cetrimide molecules are available for the interaction and the surface tension reduction becomes more gradual. With further additions of salicylic acid, the interaction probably involves mainly the cetrimide molecules in the bulk of the system. Eventually, as the degree of interaction approaches its maximum, *i.e.*, most of the surfactant molecules have interacted with the acid, the surface activity of the system appears to reach its highest level and, thereafter, the surface tension increases.

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<sup>3</sup> Cambridge Instrument Co., England.